Journal of Ceramic Processing Research. Vol. 17, No. 4, pp. 369~372 (2016)

JOURNAL OF
Ceramic
Processing Research

Detection of the third transition of InAs/GaAsSb quantum dots

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The optical properties of InAs quantum dots (QDs) embedded in $GaAs_{0.92}Sb_{0.08}$ barriers have been studied. The samples studied consist of 20 multiple layers of InAs QDs embedded in $GaAs_{0.92}Sb_{0.08}$, with each QD/barrier system separated by a 100 nm GaAs spacer. No appreciable changes in the QD properties, such as size, shape, and density, are observed by Scanning Transmission Electron Microscopy (STEM) images. The δ-doping plane beneath the InAs QDs allows the occupancy of the QD electronic sub-band states to be controlled. Low temperature (77 K) Fourier Transformation-Infrared Spectroscopy (FT-IR) results, using a multiple internal reflection (MIR) technique to enhance the optical path length, show intersubband absorption in the InAs QD area. The broad peak observed around 240 meV corresponds to the energy separation between the electron ground state and the continuum state of the QDs. Another broad peak around 440 meV is ascribed to a transition between a deep level and shallow donor level due to δ-doping as the signal increases as the doping density increases. Band structure calculations using an eight band *k·p* method are used to confirm the experimental results observed here.

Key words: Epitaxial layers, III-V semiconductor materials, Photovoltaic cells, Semiconductor nanostructures.

Introduction

InAs quantum dots (QDs) have attracted great attention as a candidate of intermediate band solar cells (IBSCs) [1, 2]. In order to realize IBSCs with the InAs QDs, it is required to simultaneously achieve high density and uniformity of QDs for the high light absorption [3]. According to our previous work InAs/GaAsSb is one of the most promising material systems since it has small valence band offset (VBO) and gives good QD properties such as small size, high density, and uniformity by Sb content [3, 4]. At this point, it is crucial to investigate optical properties of InAs/GaAsSb to obtain the band structure of InAs/GaAsSb. Especially, we have focused on electronic states in the conduction band offset (CBO) which correspond to an intermediate band in the device standpoint [5]. Since electronic states in the CBO are initially empty it is also important to control the occupancy of subband levels to make three transitions rates, valence to conduction band (E_{CV}), valence to intermediate band (E_{IV}), and intermediate to conduction band (E_{CI}), comparable as shown in Fig. 1. In general, half filled intermediate levels are thought to be the optimum performance of the IBSCs [2]. Thus, a δ-doped layer with the carrier density, which is comparable with QD number density, beneath a QD plane is precisely incorporated as a carrier supplier [5, 6]. The more population of carriers induced by the δ-doped layer holds the carriers more tightly in the recombination center due to the enhancement of Coulombic interaction [7, 8]. The InAs/GaAsSb with various doping levels has been characterized by low temperature photoluminescence (PL) and time-resolved PL [9]. The PL data show that the δ-doping plane can play a role of controlling the occupation of electronic levels in the CBO by increasing the possibility of the emission from the first excited states (E1H1) [5, 6].

20 multiple layers of InAs/GaAsSb separated by a thick GaAs spacer (100 nm) are grown to enhance light absorption in the QD area without changing QD properties such as size, shape, and density. Various δ-

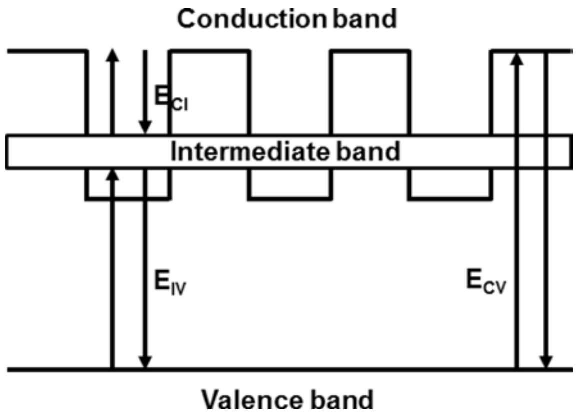

Fig. 1. Schematic diagram for possible three transitions of the intermediate band solar cells.

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doping density beneath InAs QDs is introduced to occupy QD electronic sub-band states. Intersubband transitions corresponding to the third transition of InAs/GaAsSb material system are experimentally determined by low temperature (77 K) Fourier Transformation-Infrared Spectroscopy (FT-IR) using a multiple internal reflection (MIR) technique. It is noted that a broad peak around about 240 meV corresponding to the energy separation between the electron ground state and the continuum state of the QD is observed. Another broad peak around 440 meV originates from a transition between a deep level and shallow donor level introduced with increasing of δ-doping density. The band structure based upon an eight band *k·p* method confirms the experimental results observed here. All related physical phenomena are discussed as well.

Experimental Procedure

All sample structures are grown in an Applied Epi Gen III MBE system. After observing de-oxidation of semi-insulating GaAs (001) substrate the temperature is set to 580 °C and a GaAs buffer layer (200 nm) is grown. The temperature is then decreased to 500 °C and following the growth of 5 nm of GaAs, a 17 nm GaAsSb layer with 8% Sb composition is grown. Following a pre-doping rest of 5 s under an As overpressure, a δ-doped layer is created by depositing silicon (Si) for an exposure time of 0, 3, 7, and 11 s, respectively, with the Si source temperature set to 1200 °C [3]. This process is immediately followed by the growth of a 3 nm $GaAs_{0.92}Sb_{0.08}$ layer. InAs QDs (2 MLs) are then formed on the $GaAs_{0.92}Sb_{0.08}$ barrier layer and capped by 20 nm of $GaAs_{0.92}Sb_{0.08}$ all at a growth temperature of 500 °C. A 100 nm thick GaAs spacer is then grown at 580 °C before another InAs/GaAsSb structure is repeated. In total there are 20 InAs/GaAsSb multiple layer structures grown, in order to increase absorption cross-section of the InAs QDs for FT-IR absorption measurements. The 100 nm GaAs grown between the GaAsSb/InAs/GaAsSb layers is to ensure that there is no accumulation of compressive strain as the number of QD layers increases and so reduce likelihood of dislocations forming. Atomic Force Microscope (AFM) scans of uncapped QD samples indicate the QD density to be $4.5 \times 10^{10}\,cm^{-2}$, with the lateral size and height of QDs found to be approximately 23.4 nm and 4.3 nm, respectively [5]. Using these results, the δ-doping levels are tuned so that the electronic subband levels of the QDs are occupied by 1.5, 3.5, and 5.5 electrons, respectively. Bright field Scanning Transmission Electron Microscope (STEM) is used to observe the variation of size and shape for each layer of the InAs QDs. Low temperature (10 K) photoluminescence (PL) measurements and near infrared absorption spectrometry at room temperature are performed to observe the QD emission wavelengths and absorption spectra for single and 20 multiple InAs QDs (MQDs), respectively. The FT-IR is equipped with a liquid nitrogen cryostat and liquid nitride cooled mercury cadmium telluride (MCT) photodiode as well as a polarizer for p-polarization set in front of the incident light. The edges of the InAs MQD samples are grinded and polished to obtain 45 degree facets in order that incident light can be multiply bounced inside the samples (please see Figure 2) and that ensure that the optical path length is enhanced leading to greater absorption by the QDs.

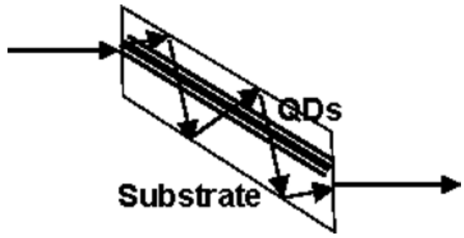

Fig. 2. Sample configuration for FT-IR measurement using a multiple internal reflection technique.

Results and Discussion

Fig. 3(a) and (b) display cross-sectional bright field STEM images of the samples containing 20 multiple InAs QD layers with 17 QD layers clearly observable in Fig. 3(a), whereas the remaining 3 QD layers are dimly observed in the bottom of the image. The GaAsSb layers containing the QDs correspond to the bright lines marked by the red arrows, with the darker areas corresponding to the 100 nm GaAs spacer layers. It is found that the QDs in adjacent layers are not vertically aligned along the growth direction. High-resolution (HR) STEM images such as those shown on Fig. 3(b) and 3(c) for the 3rd and 15th layers, respectively, allow the dimensions of the QDs in different layers to be compared. It is found that the average size of the QDs in all of the layers studied by HR STEM is roughly 24 nm wide and 4 nm high, corresponding well to the results found for a single QD layer (23.4 nm and 4.3 nm). It is therefore concluded that the 100 nm GaAs spacer layer has ensured that there are no strain interactions between the

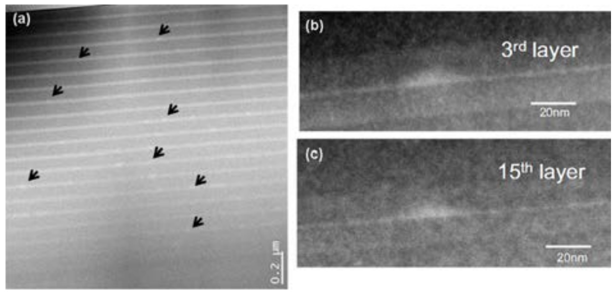

Fig. 3. Cross-sectional bright-field STEM images of 20 multiple stacks of InAs QDs embedded in GaAsSb (a) and singe InAs QD taken from 3rd (b) and 15th (c) layers.

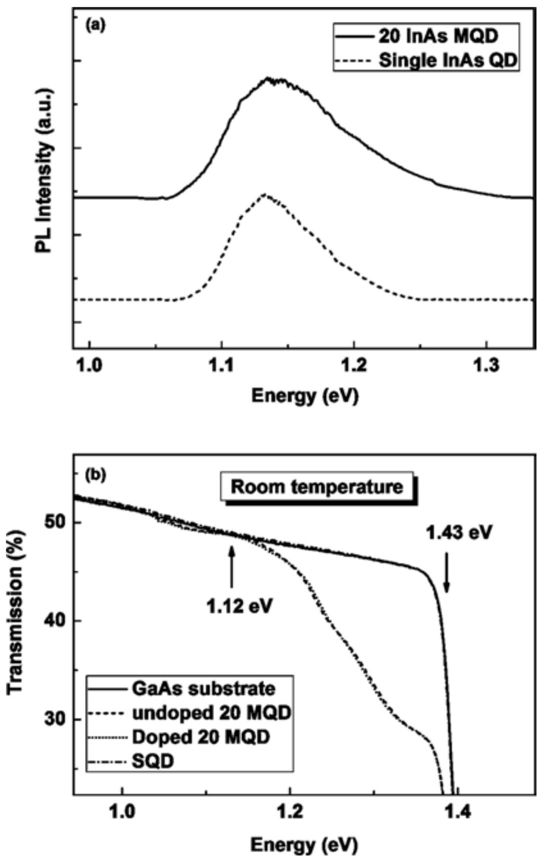

Fig. 4. (a) PL spectra at 10 K of single InAs QD (SQD) and 20 multiple quantum dots (MQD) and (b) absorption spectra at room temperature of GaAs substrate, undoped and doped 20 MQDs, and SQD.

adjacent QD layers since none of the layer appears to have a distorted QD size distribution and no vertical alignment observed.

This observation is further confirmed by the PL spectra in Fig. 4(a) for a single QD layer sample and a sample with 20 QD layers, with the peak emission energies being 1.136 eV and 1.14 eV, respectively. This suggests that the average QD size has not changed with the addition of further QD layers, and no significant change in the full-width-at-half-maximum (FWHM) value means that the QD layers grown have similar size distributions as well as the same average size. The effect on the absorption of including a large number of QD layers is clearly observable in the absorption spectra presented in Fig. 4(b), with results from a GaAs substrate (reference), single QD (SQD), and undoped and doped (5.5 e/dot) 20 multiple stacks of QDs. These results indicate that the single QD sample does not absorb appreciable light with energy below GaAs band gap as its absorption spectrum can not be distinguished from the GaAs reference spectrum. For both of the samples containing 20 layers of QDs appreciable light absorption takes place from an energy of approximately 1.12 eV as shown in Fig. 4(b). These results confirm that the inclusion of 20 layers of QDs provides a substantial enhancement in the sub-bandgap photon absorption.

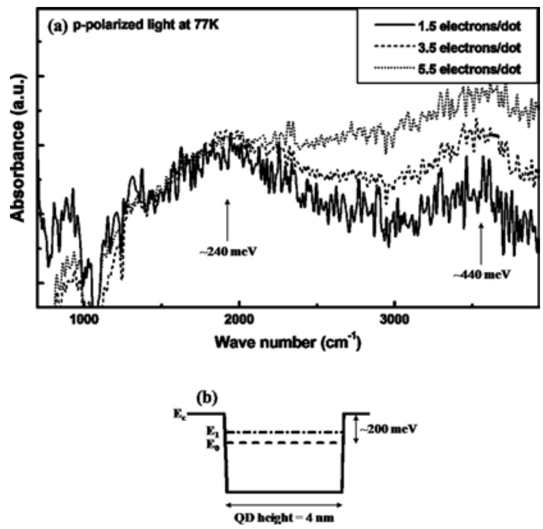

Fig. 5. (a) FT-IR spectra at 77 K of 20 InAs MQDs embedded in GaAsSb as a function of δ-doping density using a multiple internal reflection technique and (b) conduction band structure of GaAsSb/InAs QD/GaAsSb system at 0 K. (E_0 and E_1 denote electron ground state and first excited state, respectively.)

FT-IR spectra at 77 K for samples containing 20 QD layers embedded in GaAsSb, with δ-doping density of 1.5, 3.5, and 5.5 e/dot, are presented in Fig. 5(a). As well as using the MIR technique outlined earlier to enhance absorption a polarizer is utilized to obtain p-polarized incident light since the p-polarized light has an electric field component normal to a growth direction of samples, which should help the light absorption further since the InAs QDs have greater quantum confinement along the growth direction due to their anisotropic aspect of dots. The FT-IR spectrum of the undoped InAs MQDs is taken as the background and subtracted from the spectra obtained for the rest of the samples. It is revealed that there is a broad peak around approximately 240 meV with a FWHM of ~ 96 meV for all of the doped samples, with the peak signal very similar for all of the samples and another broad peak around 440 meV that is seen to increase with the δ-doping level.

The peak observed around 240 meV for all of the δ-doped samples is ascribed to absorption between the confined states of the QDs and the band edges of the GaAsSb barrier layers. When these results are compared to the reported values from multiple layers of InAs/GaAs QDs [1] (absorption peak energy = ~ 190 meV and FWHM = 120 meV), our absorption energy and FWHM are greater and narrower, respectively. This is attributed to the introduction of GaAsSb barriers since GaAsSb improves the QD uniformity and thus reduces the FWHM, and shifts the conduction band edge up with respect to the InAs leading to increasing the electron confinement energy [3, 4]. The peak around 440 meV is ascribed to a transition between a deep level and shallow donor level introduced by the δ-doped layer since it can be seen to increase with the δ-doping density [2].

The energy band structure (0 K) of GaAsSb/InAs QD/GaAsSb system is calculated to confirm the observed experimental data. The band alignments at the Γ point are determined by implementing the model-solid theory to calculate the elastic strain distribution around the QDs using the continuum theory of elasticity [3, 4]. Using the resulting strain distribution to derive the strained band structure, the subband electron and hole confined levels in the QD are evaluated by the single band constant potential method [3]. As can be seen from Fig. 5(b), the value found from our band calculations for the intersubband transition between the confined electron QD ground state and GaAsSb barrier continuum state is ~ 200 meV slightly lower than the value obtained from the observed experimental data (~ 240 meV). This difference can be attributed to the temperature of the measurements being higher than those of the calculations, since as explained in [10] the higher temperature means that smaller QDs (meaning smaller confinement energy) can be depopulated by thermionic emission. This would mean that the majority of absorption is by larger QDs with larger confinement energy and hence absorption is seen at a higher energy.

The results presented here suggest that it is possible to observe the third transition in an IBSC by monitoring the absorption corresponding to the intersubband transition between QD confined states and barrier continuum states. The intersubband transition of InAs/GaAsSb observed in these measurements, corresponding to the third transition, is hard to observe due to low oscillator strength as well as low absorption cross-section. Nevertheless, the increased number of QD layers and the use of the MIR technique in conjunction with low temperature FT-IR measurements along with p-polarized light allow the intersubband transition of InAs/GaAsSb to be observed. Since there is no substantial alteration of the band structure caused by the growth of multiple QD layers from single QD sample, this provides one with more energy ratio among three transitions to estimate the efficiency of IBSC fabricated with practical material combinations.

Conclusions

We have studied the intersubband transition of 20 multiple InAs/GaAsSb QDs by FT-IR measurement with the MIR technique. The results presented here indicate that 20 multiple layers of InAs/GaAsSb are successfully grown for the enhancement of light absorption in the QD area without introduction of QD size changes. The electronic levels of InAs QDs are controlled by the introduction of various δ-doping density beneath the InAs QDs. FT-IR measurement for 20 MQDs shows the intersubband transitions of InAs/GaAsSb around ~ 240 meV corresponding to the third transition by using a multiple internal reflection (MIR) technique. Another peak observed around ~ 440 meV is shown due to the introduction of defects induced by δ-doping. Since the energy of the third transition of our candidate material is experimentally measured, our findings presented here open the way to estimate the efficiency of IBSCs which is closer to the practical values.

Acknowledgments

We gratefully acknowledge Dr. Stephen Hegedus and Dan Ryan at the Institute of Energy Conversion, University of Delaware, and the LeRoy Eyring Center for Solid State Science at Arizona State University for help with the near infrared absorption spectrometry and the use of TEM and PL, respectively. In addition, it is gracious to acknowledge Nutan Gautam and Dr. Sanjay Krishna at Center for High Tech Materials at University of New Mexico for the use of FT-IR.

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